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LITHIUM ANODE LIMITED CYCLE  
BATTERY INVESTIGATION

Quarterly Technical Progress

Report No. 6

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Lockheed Palo Alto Research Laboratory

Palo Alto, California

Prepared by:

H. F. Bauman, Staff Scientist  
J. E. Chilton, Research Scientist  
A. E. Huitquist, Research Scientist  
Materials Sciences Laboratory  
Electrochemistry

Approved by:

G. B. Adams, Senior Member  
Materials Sciences Laboratory  
Electrochemistry

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## FOREWORD

The work described in this report was accomplished in the Electrochemistry group, Materials Sciences Laboratory, Lockheed Palo Alto Research Laboratory, Palo Alto, California, for the Air Force Aero Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, United States Air Force, Wright-Patterson Air Force Base, Ohio, on Contract No. AF 33(615)-2455, Task 817304-20. Mr. W. S. Bishop of the AF Aero Propulsion Laboratory is project engineer for the project. This report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

## ABSTRACT

The purpose of this experimental program is to develop technology sufficient to construct batteries based on the lithium-cupric fluoride couple. During this period, separator material with a resistance of less than  $1.0 \Omega/\text{in.}^2$  has been evaluated and sheet lithium electrodes have been discharged anodically for 100 hr at  $10 \text{ mA}/\text{in.}^2$  with less than 100 mV polarization. Both of these items are milestones of this contract.

Aluminum cased cells have been constructed that have delivered 32.2 A-hr to a 2.0-V endpoint and had an energy to weight ratio of 72.5 W-hr/lb of total cell weight. In these aluminum cased cells which are better sealed than the plastic cells used in preliminary tests, low water content in the cell becomes very important. Water introduced in the electrolyte, cathode preparation or separator reacts with the lithium to form hydrogen. Pressure from the gas evolution distorts the metal case and the resulting movement and misalignment can result in shorting the active elements of the cell. Water in the cupric fluoride used in cathodes in cells does result in higher voltage discharges, possibly because the resulting soluble copper species gives a lower effective current density.

A 30-V battery was assembled from aluminum cell which failed presumably because of water introduced by the electrolyte. This battery which weighed 9.2 lb was designed to deliver in excess of 25 A-hr during a 100-hr discharge. It delivered 9 A-hr and with an energy to weight figure of 24.5 W-hr/lb to a 22.0-V endpoint.

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Section 1  
INTRODUCTION

This is the sixth quarterly technical progress report of this program to develop high specific energy systems based on the lithium-cupric fluoride and the lithium-cobalt fluoride couples. Work with the latter couple has been stopped because of the low efficiency and the poor voltage regulation exhibited by cells based on that system. The lithium-cupric fluoride couple has a theoretical energy to weight ratio of 746 W-hr/lb which makes its development of interest as a power source for space vehicles.

The goal of this program is the assembly and test of 1500 A-hr batteries delivering 150 W-hr/lb. As an interim step, aluminum cased cells of 25 A-hr nominal capacity are being constructed. Previous work has been concerned with the optimizations of the electrolyte, anode, separator material, and the cathode structure. The cathode structure is the limiting element in the cell at the present time and additional development work is required for its improvement.

## Section 2

### EXPERIMENTAL WORK AND DISCUSSION

#### 2.1 SEPARATOR EVALUATION AND TEST

It is desired that separator materials be found that have as low a resistance as possible compatible with chemical and mechanical requirements of the system and one of the goals of this work is to find a separator less than 0.010 in. thick and with a resistance of less than  $1 \Omega/\text{in.}^2$ . All the materials investigated this month were of synthetic resin or glass fibers matted in non-woven paper form. A saturated solution of  $\text{NH}_4\text{PF}_6$  in butyrolactone (16.4 g in 100 ml) which had a specific conductivity of  $1.7 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$  at  $24^\circ \text{C}$  was chosen as the electrolyte. Electrical values were determined in a Teflon fixture with two 1-in diameter parallel silver faces. The wet separator was positioned between the fixtures and the dissipation factor and the series capacitance measured with a 1000-Hz bridge. Series resistance values were calculated from the formula  $R_s = D/wC_s$  in the case of material with a low dissipation factor or from the formula  $R_p = 1/wC_p D$ ,  $R_s = [D^2/(1 + D^2)]R_p$  in the case of material with a high dissipation factor. The calculated values for the material tested are shown in Table 1. Polyester material E 458 was found to have a resistance of less than  $1 \Omega/\text{in.}^2$  and to be less than 0.010 in. thick, fulfilling one of the contract goals.

#### 2.2 ELECTROLYTE EXPERIMENTS

##### 2.2.1 Solubility of $\text{CuF}_2$ in Electrolyte

Analysis of copper ion content and of water content of a 1 M  $\text{LiClO}_4$ -propylene carbonate (PC) solution saturated with copper fluoride was performed. The solutions thus prepared with this cell electrolyte would approximate the conditions which are encountered in a working cell. The analysis of water and of copper ion would indicate

Table 1  
CALCULATED A-C RESISTANCE OF SEPARATOR MATERIALS  
Electrolyte:  $\text{NH}_4\text{PF}_6$  (sat.) in butyrolactone

Material	Manufacturer	Code	Thickness (in.)		Resistance ( $\Omega/\text{in.}^2$ )
			Wet	Dry	
Polyester	KM	EM371	0.005	0.004	7.30
Polyester	KM	M1481	0.008	0.005	2.51
Polyester	KM	M1430	0.001	0.001	1.76
Polyester	KM	M1435	0.003	0.001	4.81
Polyester	KM	M1471	0.005	0.004	2.22
Polyester	KM	EM415	0.004	0.002	5.95
Polyester	KM	M1434	0.004	0.003	2.10
Polyester	KM	EM474	0.008	0.006	3.07
Polyester	KM	M1414	0.002	0.001	1.51 <sup>(a)</sup>
Polyester	KM	M1445	0.005	0.003	2.07
Polyester	KM	EM458	0.003	0.002	0.96 <sup>(a)</sup>
Glass	RA	934HA	0.011	0.010	1.75
Glass	KB	PM6615	0.010	0.010	1.77
Polypropylene	PC	FT2140	0.012	0.011	2.27
Rayon	KM	M92	0.002	0.002	2.22

(a) Measured at 35° C.

the concentration of reactable species which would remove lithium metal by reaction to form either hydrogen gas or copper metal. Long-term wet cell ( $\text{Li-CuF}_2$ ) stability would be expected only for electrolytes containing a minimum amount of such reactable species. Samples were prepared with 5-g lots of the following materials: anhydrous copper fluoride from Source B-Lot Z 103, anhydrous copper fluoride from Source A-Lot 2, and copper fluoride dihydrate prepared by reaction of copper basic carbonate with excess hydrofluoric acid. The solids were placed in glass ampules, 50 ml of the 1 M lithium perchlorate-propylene carbonate electrolyte added and the ampules flame-sealed. After a stand time of 31 days, during which time the samples were intermittently

shaken, the ampules were opened and the clear supernatant liquid removed for analysis. Copper ion was determined by reaction with iodide ion and by titration of the resulting iodine by standard sodium thiosulfate solution. Water was determined by titration with a Karl Fisher reagent, correcting the value found for the amount of copper present, since copper reacts with the Karl Fisher reagent to produce iodine. The results of the analysis are presented in Table 2.

Table 2  
SOLUBILITY OF  $\text{CuF}_2$  IN LITHIUM PERCHLORATE-PROPYLENE  
CARBONATE ELECTROLYTE

Copper Fluoride	Water M <sup>(a)</sup>	Water (ppm)	Copper M <sup>(a)</sup>	Solution Color
Electrolyte (1 M $\text{LiClO}_4$ -PC)	0.0099	148	0	None
Anhydrous $\text{CuF}_2$ , Source B Lot Z 103	0.0173	258	0.008	Light greenish yellow
Anhydrous $\text{CuF}_2$ , Source A Lot 2	0.0194	2,900	0.0616	Light green
$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$	0.705	12,000	0.174	Blue green

(a) M = moles/liter solution.

The water content of the electrolyte was 148 ppm. Since the propylene carbonate as distilled is 20 ppm water, the original water content of the dried lithium perchlorate was less than 0.1%. Water found in the electrolyte from Source B  $\text{CuF}_2$  was 258 ppm of which less than half represents water extracted from the  $\text{CuF}_2$  anhydrous with the bulk of the water coming from the electrolyte. Water found in the electrolyte from Source A  $\text{CuF}_2$  was much greater, being 2,900 ppm and there was a corresponding much greater copper ion solubility. The water content determined by this test is not necessarily equivalent to the water content of the original anhydrous solid materials since only water in solution was determined and water of crystallization could still be present in the solid state. This is demonstrated by the water determination with copper fluoride dihydrate where less than half of the water was found in soluble state in the electrolyte.

### 2.2.2 Spectrographic Analysis of Electrolyte

The many bands due to water and hydroxyl groups present in the infrared region of the electromagnetic spectrum presented a method of analyzing the solvent and electrolyte for water. Practically, this has been used as a routine analysis in the control of organic solvent production. The technique has utilized the OH stretch band positioned at  $3600\text{ cm}^{-1}$  for the most part, but occasionally the first overtones of the water absorption bands found between about  $6200$  and  $8000\text{ cm}^{-1}$  have been used. These analyses have been used in place of the Karl Fischer reagent where the latter is subject to unstable endpoints and to study the effect of acid concentration on these absorption band and to determine the bonding of the water to the organic.

Initial attempts at water analysis of the solvent propylene carbonate were made using the Perkin Elmer Infrared Spectrophotometer Model 221. This instrument was used to examine the OH stretch band at  $3600\text{ cm}^{-1}$  using  $0.1\text{ mm}$  NaCl cells. The peak height was measured relative to the minimum absorptance at  $3750\text{ cm}^{-1}$ . Data from two samples spiked with known amounts of water and from other samples examined are shown in Table 3.

Table 3  
INTENSITY OF  $3600\text{ cm}^{-1}$  BAND

Experiment	Sample Description	Peak Height	Remarks
1	1A Solvent, as-received	50.5	Peak broadened due to additional peak developing at $3650\text{ cm}^{-1}$ .
	B Solvent, distilled	36.5	
	C Solvent and 4000 ppm $\text{H}_2\text{O}$	41.5	
2	A Solvent, distilled	39	
	B Solvent and 200 ppm $\text{H}_2\text{O}$	46	

The reduction in absorptance as a result of distillation agrees with the observed reduction in water content, as does the increase in absorptance as the result of spiking the solvent with 200 ppm water. However, the increase in absorptance is not large

enough to be of value in determining small amounts of water. Larger amounts of water does not increase the absorptance of this peak appreciably but apparently produces new peaks which indicates that the additional water is bound to or interacts with the solvent in a different manner. The spectra of the pure distilled solvent observed in this study are identical to those published by Sadtler.\* The results observed here indicated that the determination of water in this solvent using this band was not feasible.

A recent publication by Karyakin and Petrov\*\* described a study of the spectra of acetone containing both water and HCl. The study used primarily infrared region between 1.3 and 1.6  $\mu$  which contains the first overtones of the water spectra. The particular interesting result showed that the second solute modified the water spectra by formation and hydration of the hydronium ion,  $H_3O^+$ . Thus any quantitative determination of the water present in an organic solvent is immediately affected by the presence of ions that will form hydration sheaths or will compete with water for bonding with the organic solvent. Thus, the observed peak heights become functions of both solute concentrations.

Despite the forecast complications, the spectra of the solvent was obtained from 2.8 to 1.1  $\mu$  on the Beckman DK-2 Recording Spectrophotometer. Using 5 cm cells, the peak height of the band at 1.875  $\mu$  was observed to be a function of the water content. The results are shown in Fig. 1 where the absorptance is plotted as a function of the water content in ppm as determined by independent measurements using the Karl Fisher Reagent. The lower limit of detectability is about 180 ppm and it would seem that the technique would be quite useful for values above this. However, water concentrations below this are undetectable and the method is of no use.

The spectra of electrolyte samples was also observed. The addition of  $LiClO_4$  to concentrations of 1.0 M so intensifies the absorption that cells of 1.0 mm or less must

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\*The Sadtler Standard Spectra, Midget Edition 3297, Sadtler Research Laboratories, Philadelphia, Pa., 1962.

\*\*A. V. Karyakin and A. V. Petrov, Zhur. Analytical Khim 19 (12) 1382, 1964.

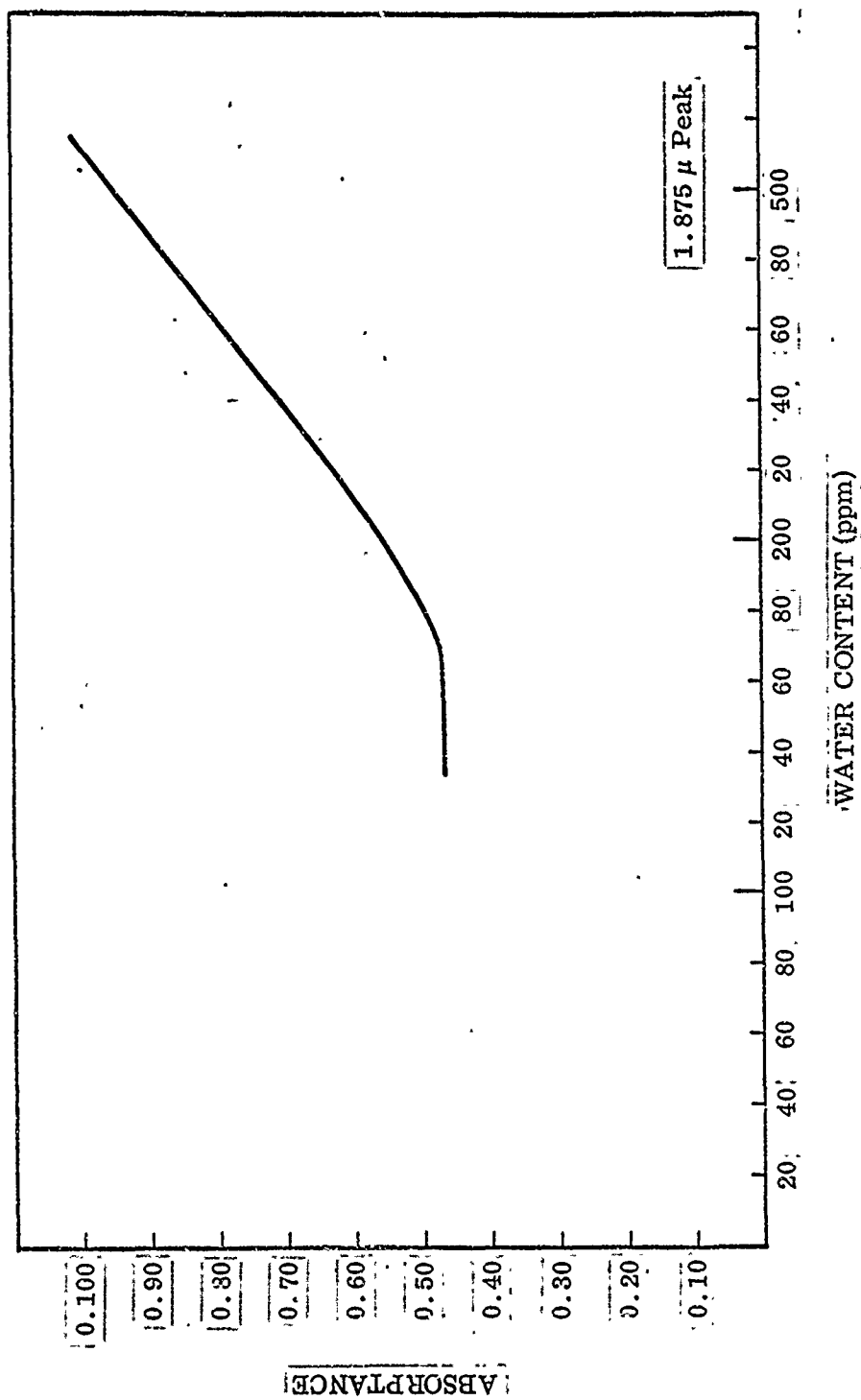


Fig. 1 Relationship of Water Content on Absorbance of Propylene Carbonate



be used in order to see the bands. The effect of water in concentrations of 500 ppm or less on the absorptance using this path length is virtually zero.

From these observations, it has been concluded that the infrared analysis of the electrolyte for water is not feasible. The pure solvent can be analyzed for water in excess of 150 ppm, by using the band at  $1.875 \mu$ .

## 2.3 CUPRIC FLUORIDE STUDY

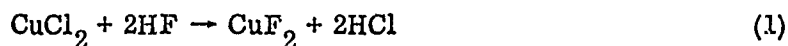
### 2.3.1 Literature Survey

Four cupric fluoride compounds in different states of hydration are commonly identified in the literature. It is to be expected that more than one of these would be found in any cupric fluoride commercially available with possibly some less easily identifiable compounds. It is of interest in this program to be able to identify the material which is used for cathodes because of the effect the different species may have on the cell characteristics of discharge and wet stand as well as for control purposes when different lots of material are used. A literature search was made which concentrated on the areas of the preparation of  $\text{CuF}_2$  and its hydrates or hydroxyl fluoride compounds, and the spectra of such materials. The search has included the Chemical Abstracts, Vols. 51 through 62, and several textbooks of infrared analysis containing extended bibliographies. The major sources of the latter class are listed below; other references are included in the appendix.

1. K. E. Lawson, Infrared Absorption of Inorganic Substances, Reinhold Publishing Corp., New York, 1961
2. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, 1963
3. A. Glassner, ANL-5750, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to  $2500^\circ \text{K}$ "
4. The Sadtler Standard Spectra, Midget Edition, No. 3297, Sadtler Research Laboratories, Philadelphia, Pa., 1962

### 2.3.2 Thermodynamic Calculations

Calculation of the free energies for several reactions that might be used in preparing anhydrous copper (II) fluoride have been made. The reactions use hydrogen fluoride as a fluorinating agent rather than fluorine primarily because of the greater ease in handling HF:



Obviously considerable fluorination potential is lost, due to the stability of the hydrogen fluoride compared to the stability of the product gases, water, and HCl.

The data are presented in Table 4 for several reaction temperatures, using the data contained in Glassner (Ref. 3).<sup>\*</sup> It is quickly apparent that the only reaction that can be expected to proceed is the reaction using CuO. The experience of Flasehen and Gain (Ref. 22A) substantiates the data. The work of Haendler et al. (Ref. 5A) in preparing the fluoride by direct fluorination using F<sub>2</sub>, and the results of Ritter and Smith (Ref. 38A) in studying the kinetics of the fluorination of the oxide using fluorine gas indicate that Reaction (2) can be used provided that reaction times sufficiently long are utilized.

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<sup>\*</sup>References designated by number alone refer to those listed on p. 8; reference numbers followed by A refer to the bibliography in the appendix.

Table 4  
FREE ENERGIES OF FLUORINATION REACTIONS

Temperature (° K)	Reaction Number		
	1	2	3
300	+9.8	-10.5	+10
400	+10.6	-7.8	
500	+9.3	-5.4	+15
600	+9.2	-2.7	
700	+9.0	-0.1	
800	+8.8	+2.3	
900	+8.6	+4.6	
1000			+34

### 2.3.3 Wet Analysis of Cupric Fluoride

Wet analysis was performed on Source A and Source B cupric fluoride which had been previously tested in cell tests and analyzed by spectrographic emission and by x-ray diffraction. In addition, Source B has supplied the copper and fluorine analysis of their material which can be used to calculate the amount of cupric fluoride in the sample. Table 5 lists the analyses as received.

Table 5  
ANALYSIS OF CUPRIC FLUORIDE SAMPLES

Composition (%)	Analysis by		
	LMSC		Manufacturer
	Source A	Source B	Source B
Cu	59.0	60.4	61.25
F			36.5
Ni	0.005	0.3	
Fe	0.003	0.009	
Sn	none	none	

The amount of impurities present was much lower than indicated by emission spectroscopy. Source B  $\text{CuF}_2$  was processed in nickel equipment which accounted for its presence in the sample. Because the copper and fluorine are major constituents and present in large amounts, analyses for these elements to obtain  $\text{H}_2\text{O}$  or OH impurities by difference from the total weight is inherently difficult.

#### 2.3.4 Preparation of $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuOHF}$

An effort was made to prepare  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CuOHF}$  to be used in cell tests and for solubility tests. Preparative methods obtained from the literature (Ref. 5A) consisted of the precipitation of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  from a solution strongly acidic with HF by the addition of  $\text{CuCO}_3$  at room temperature. The crystals were washed in ethanol to remove surface water and dried over  $\text{H}_2\text{SO}_4$ ;  $\text{CuOHF}$  was prepared by boiling a suspension of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  in water for 8 hr. Subsequent x-ray diffraction photographs indicated the presence of  $\text{CuF}_2$  and  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  in the  $\text{CuOHF}$  and  $\text{CuF}_2 \cdot \text{CuOHF}$  in the  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ .

#### 2.3.5 Infrared Spectra Study of Cupric Fluoride

The infrared spectra for copper hydroxide fluoride has been studied and absorption spectra for the deformation of the hydroxide group been reported (Ref. 18A). Specially processed copper hydroxy fluoride was ground with dried KBr and pressed into a pellet. Absorption peaks were found which correspond to those reported (Ref. 18A). Prepared copper fluoride dihydrate was ground with KBr, pressed into a pellet and the absorption spectra obtained. However, because of reaction of the light blue  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  with KBr the spectrum obtained was that of black copper bromide. Various copper fluoride samples were then ground in a mortar with mineral oil, a portion placed between AgCl windows, and the infrared spectra recorded in the range  $4000$  to  $650 \text{ cm}^{-1}$  with a Perkin Elmer Infracord. The mineral oil AgCl combination gave absorption peaks at  $3000$ ,  $1460$ ,  $1380$ ,  $1180$ ,  $970$ , and  $725 \text{ cm}^{-1}$ . No absorption peaks were found from the  $\text{CuF}_2$  Source B anhydrous except those from the mineral oil-AgCl combination. Absorption peaks were found from the  $\text{CuOHF}$  material at  $3200$ ,  $2000$ ,  $1900$ ,  $1630$ , and  $990 \text{ cm}^{-1}$ .

Absorption peaks were found from the  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  material at 830, 1630, and  $3300\text{ cm}^{-1}$ . The primary peaks for analysis of copper fluoride compounds containing hydroxyl groups would be  $1900\text{ cm}^{-1}$  for  $\text{CuOHF}$  and  $1630\text{ cm}^{-1}$  for  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$ . The copper fluoride dihydrate used for analysis was prepared by reacting copper basic carbonate with excess hydrofluoric acid as previously noted. The copper hydroxy fluoride used for analysis was prepared by heating a water suspension of copper fluoride dihydrate in boiling water for 2 weeks and drying the precipitate in an oven at  $110^\circ\text{C}$ . This material was essentially free of dihydrate as contrasted with the material boiled for a shorter time. The infrared spectra measurement of copper fluoride samples can be used for a preliminary examination of impurity content.

### 2.3.6 Bag-Type Cell Tests to Evaluate Cathodes

Two groups of cells were assembled with cathodes containing  $\text{CuOHF}$  and  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  prepared as previously described. Cells from these two groups were discharged at 1.5 and  $6.0\text{ mA/in.}^2$ . The discharges at  $1.5\text{ mA/in.}^2$  are shown on Figs. 2 and 3. Both groups were characterized by extensive discharges above 3.0 V with abrupt voltage drop at the end of discharge; the discharges at the higher rate were similar but of about 20-hr duration. It should be pointed out that this batch of  $\text{CuOHF}$  had  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  as an impurity as previously noted. A subsequent preparation was substantially free of  $\text{CuF}_2 \cdot 2\text{H}_2\text{O}$  but this has not as yet been cell tested.

A second lot of  $\text{CuF}_2$  (2103) was received from Source B which was light yellow and gave an x-ray diffraction pattern only for  $\text{CuF}_2$ . This lot was used to prepare cathodes that were assembled in two sets of cells and discharged. The second batch of cells received  $15\text{ cm}^3$  of electrolyte rather than  $10\text{ cm}^3$  as it was intended that electrolyte would be removed from the cell during discharge for copper analysis. This was not possible as the electrolyte was all absorbed in the cathode and separator. The discharge of cells in the two groups is shown on Figs. 4 and 5. It will be noticed on Fig. 4 that there was poor reproducibility between cells at each current density in that the shape of the discharge curves was dissimilar. Figure 5 which shows the discharge of cells with extra electrolyte shows a consistent early drop in voltage to 2.4–2.7 V

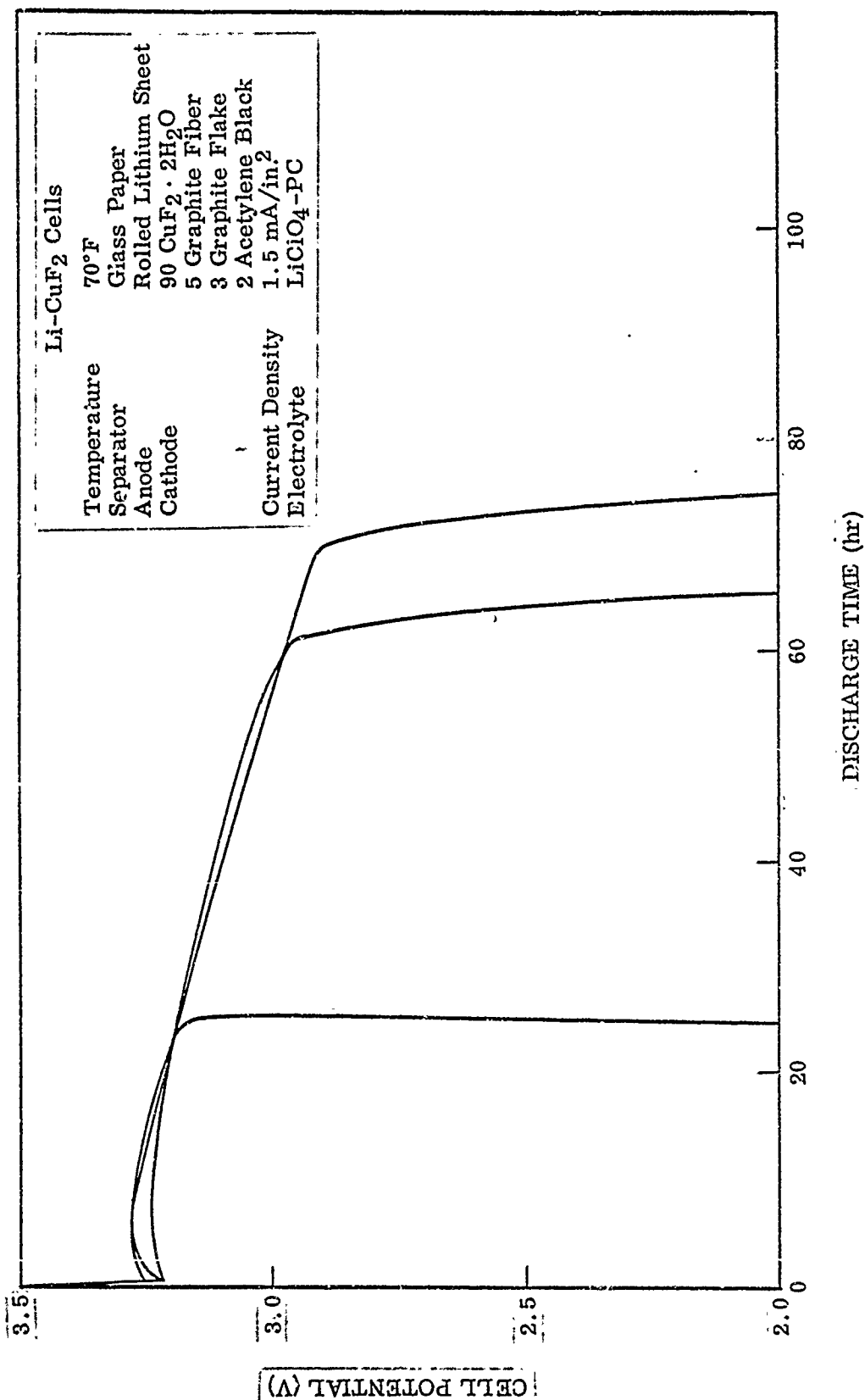


Fig. 2 Discharge of Cells With CuF<sub>2</sub> · 2H<sub>2</sub>O Cathodes

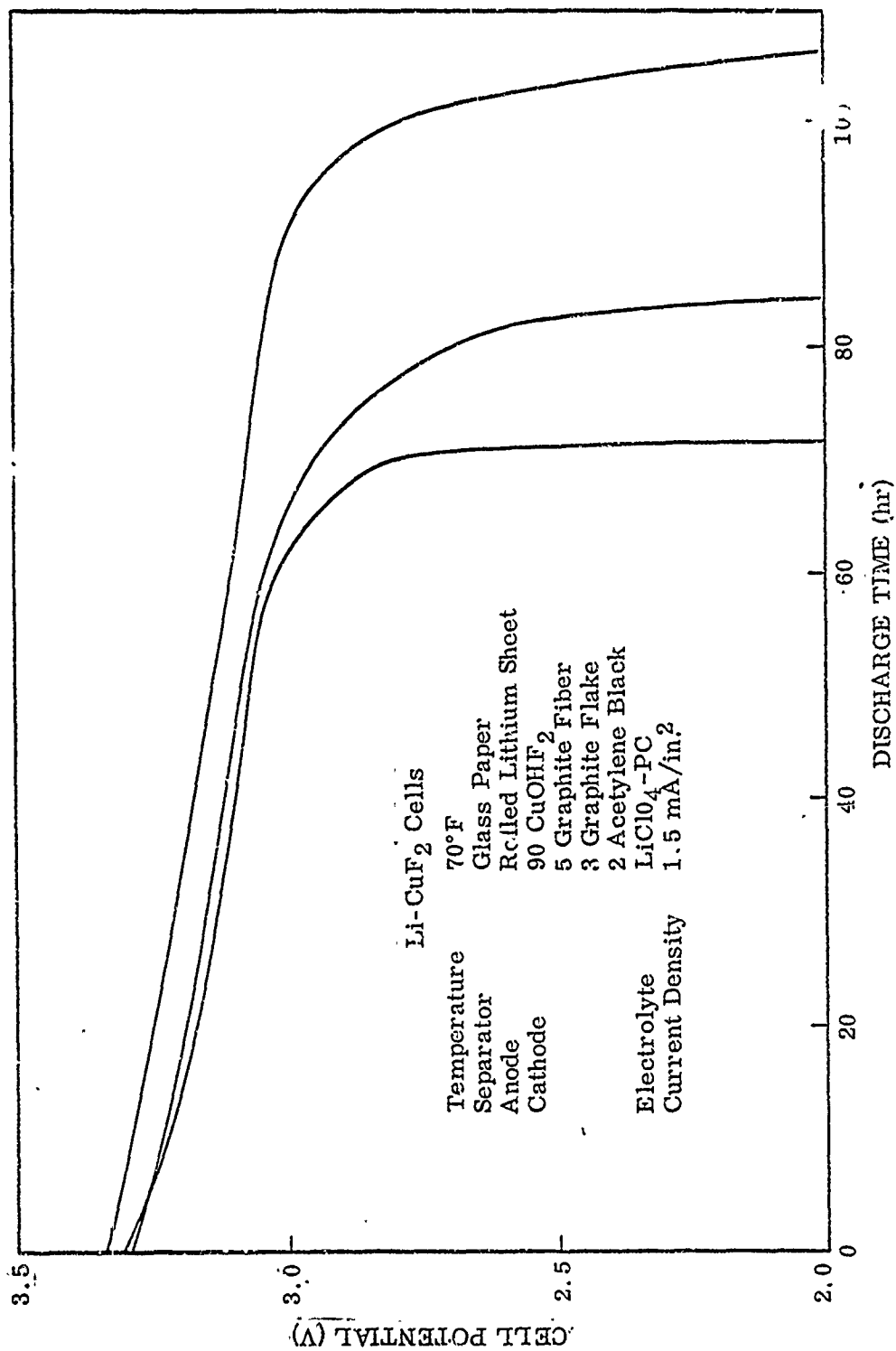


Fig. 3 Discharge of Cells With CuOHF Cathodes

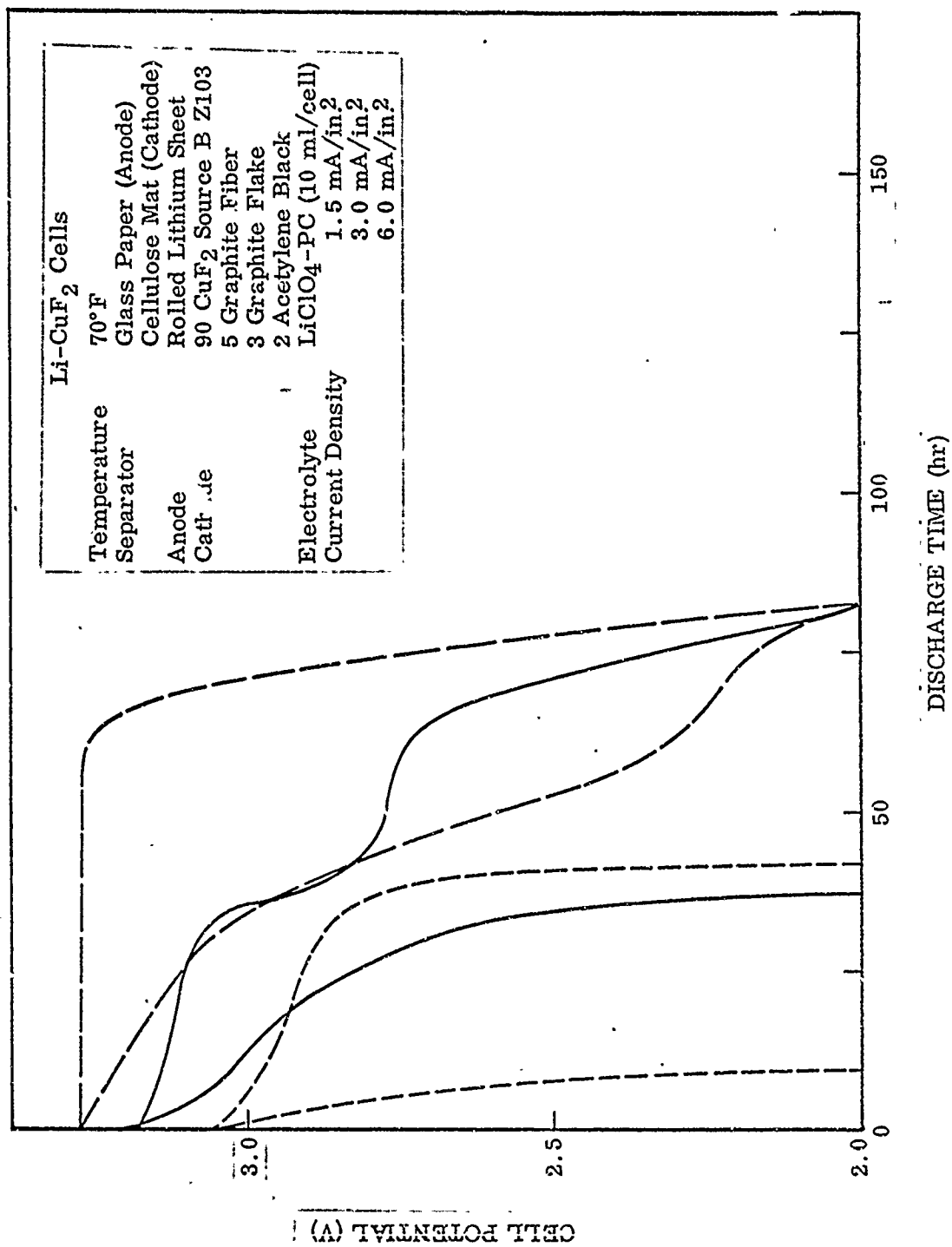


Fig. 4 Discharge of Cells With Source B Lot Z103 CuF<sub>2</sub> in Cathodes



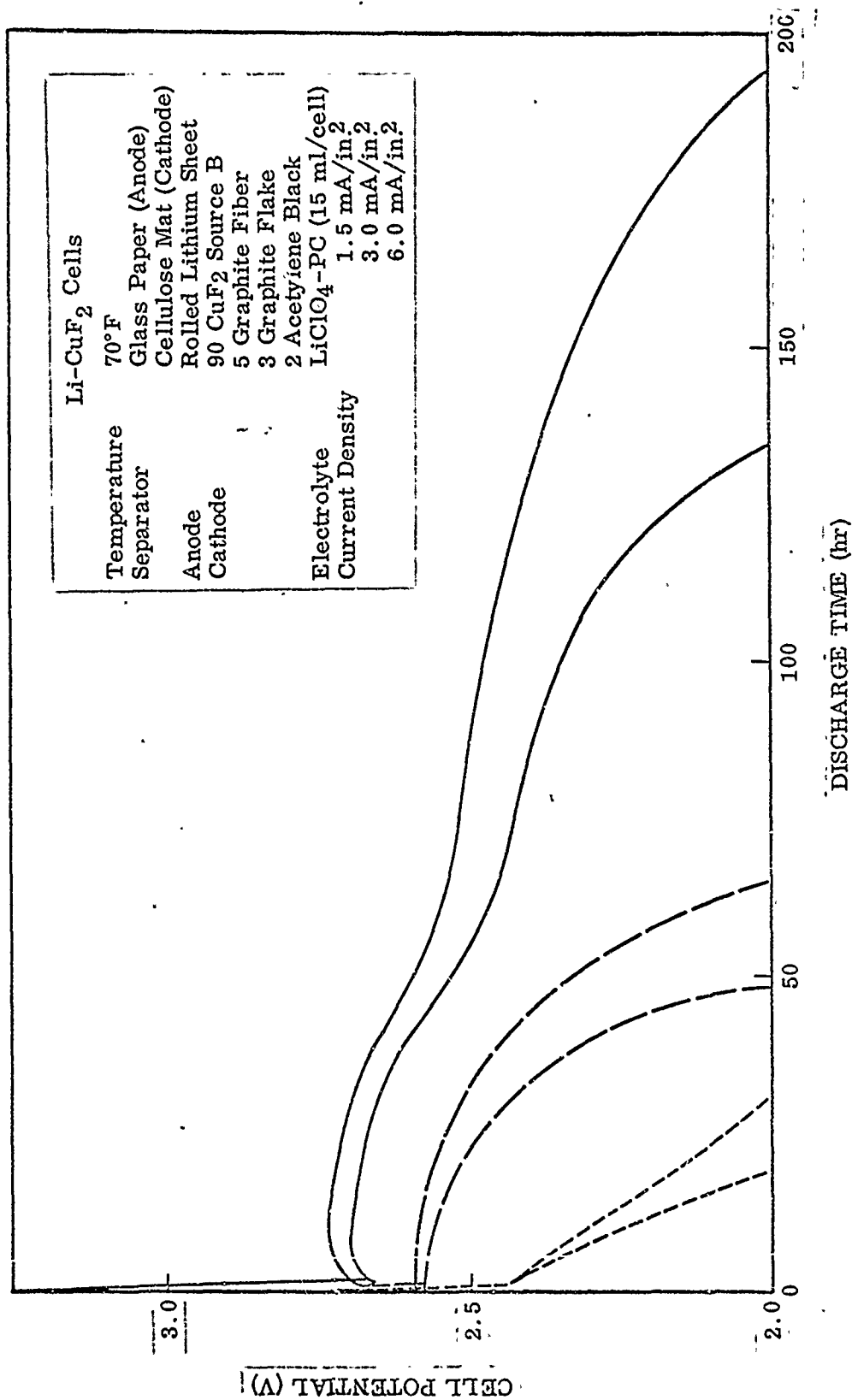


Fig. 5 Discharge of Cells With Source B Lot Z103 CuF<sub>2</sub> in Cathodes and Additional Electrolyte

followed by a long discharge plateau at this level for cells discharged at 1.5 and 3.0 mA/in.<sup>2</sup>. Further examination of construction data for the two cells showed that the cellulose separator used in the second group of cells had been oven dried before use and the cellulose separator in the first group of cells had been used as stored in the laboratory. The known differences between the two lots of cells therefore was possibly added water from the separator in the first group and additional electrolyte in the second group.

An open circuit voltage of 3.29–3.33 V was obtained for cells in the second group discharged at 1.5 and 3.0 mA/in.<sup>2</sup> when the current was interrupted for 20 hr after 40 hr of discharge. Cells discharged at 6.0 mA/in.<sup>2</sup> had been driven below 0 V at this time but recovered to voltages of 2.91 and 3.2 V.

A cathode formulation that will discharge efficiently at as high a current density as possible is desired as this reduces the number of electrodes and grids and the amount of electrolyte in the cell and thus reduces the overall inert weight. Cells were prepared in which the conductive-nonconductive material ratio in the cathodes was varied first about the present 90–10 ratio and then with increasing amounts of conductive additive. The ratio of graphite fiber, graphite flake, and acetylene black was maintained during this series of tests. The first changes about the present composition shown on Fig. 6 indicate the advantage of increasing the conductive material; Fig. 7 shows still greater improvement above 15%. An additional series of tests were made in which the acetylene black-graphite flake ratio was changed while the  $\text{CuF}_2$  was maintained at 80% and the graphite fiber at 10%. The discharges shown in Fig. 8 indicate some advantage in the increased proportion of acetylene black. Substitution of silver flake and silver powder for graphite flake in a 90%  $\text{CuF}_2$  cathode showed no improvement. All of these cell tests were made with Source B Lot Z103  $\text{CuF}_2$  and all had initial open circuit voltages of 3.40–3.45 V.

Our present belief as the result of cell tests and electrolyte analysis is that the inclusion of water in the cell, particularly in the cathode, solubilizes  $\text{CuF}_2$  sufficiently that the conductive cathode structure is less important in current collection. Soluble copper can diffuse to a reaction site which is electronically connected to the cathode

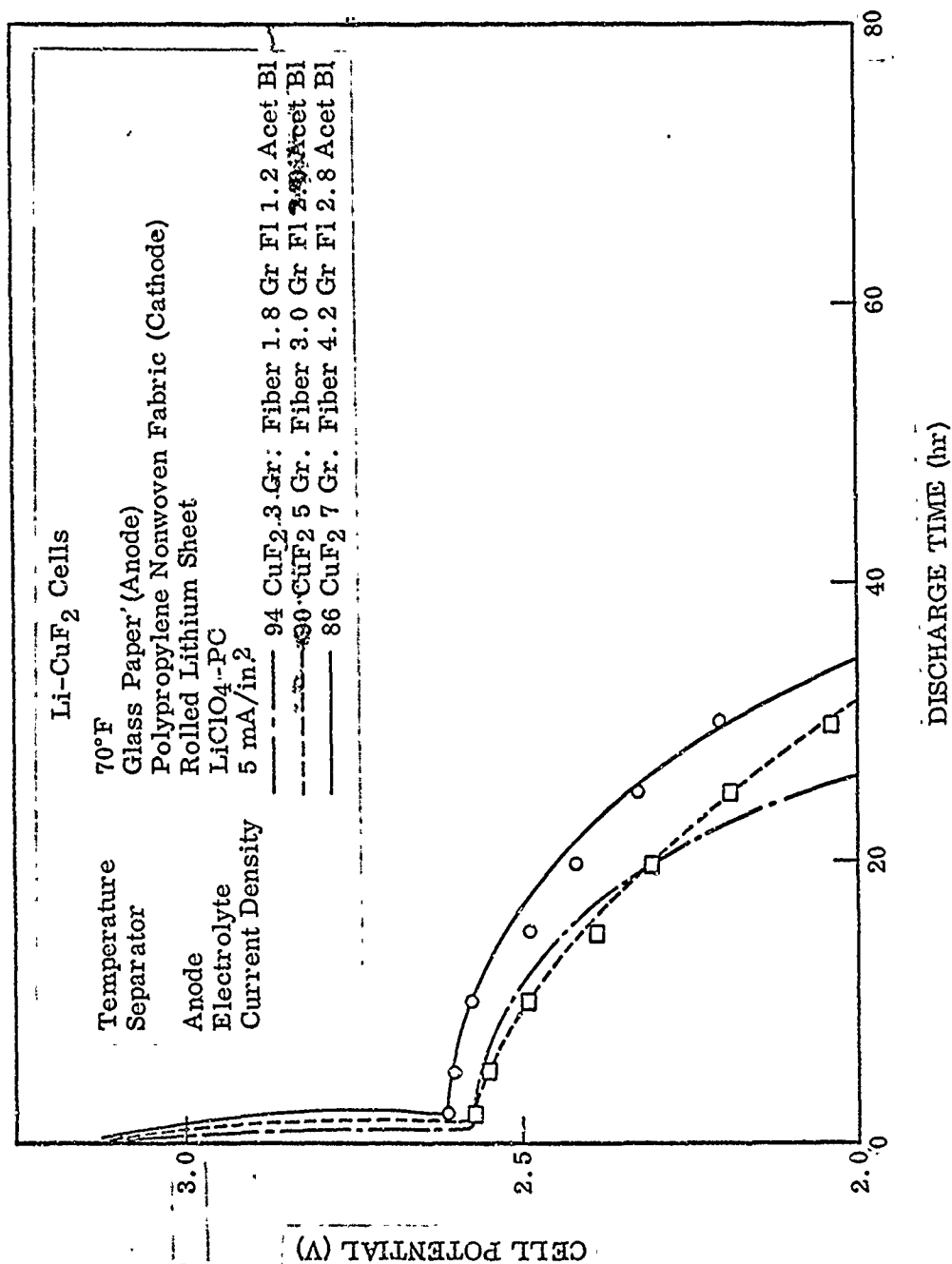


Fig. 6 Discharge of Cells With Changes of Conductive-Nonconductive Ratio in the Cathodes

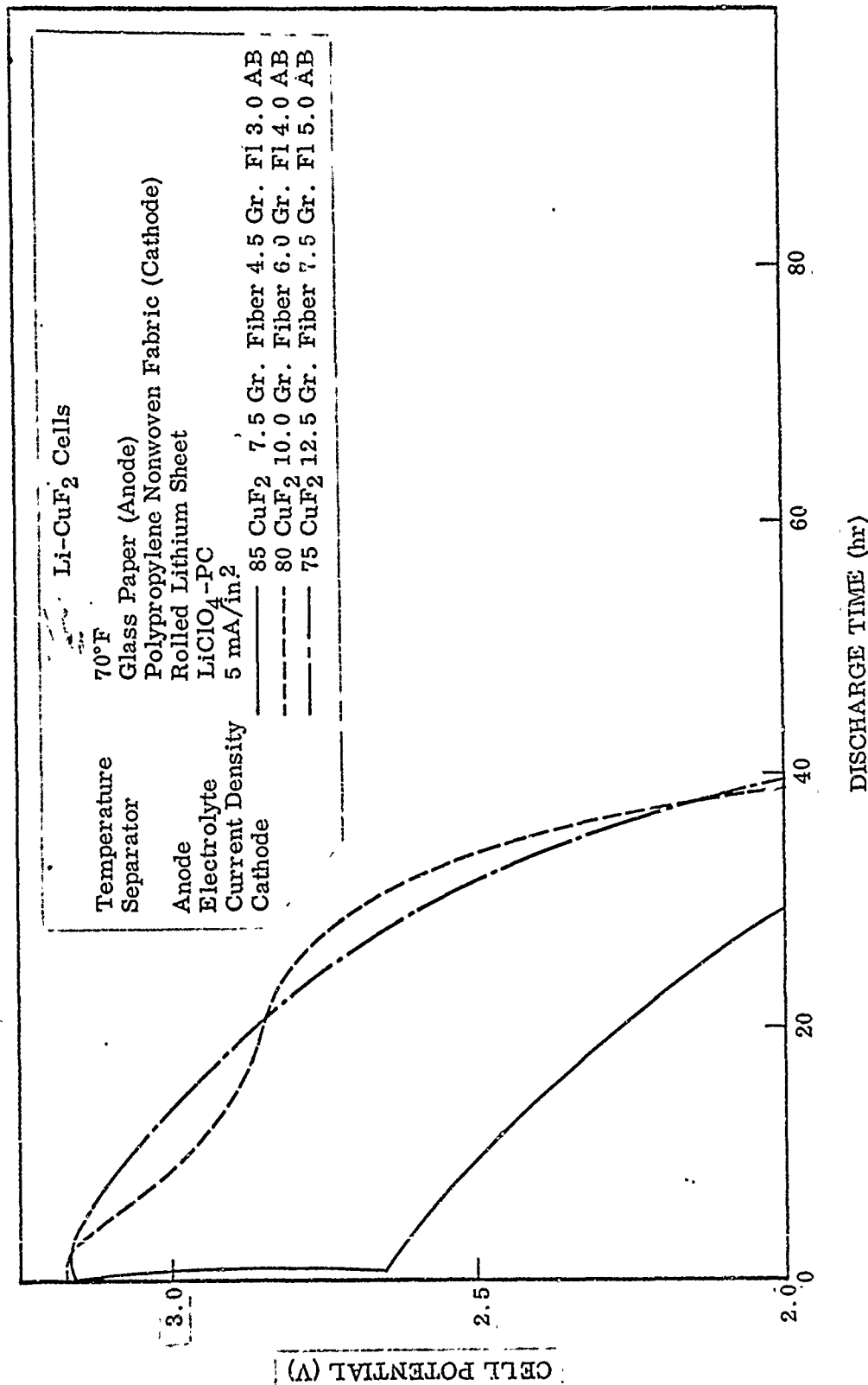


Fig. 7 Discharge of Cells With Increased Amounts of Conductive Additive in the Cathode

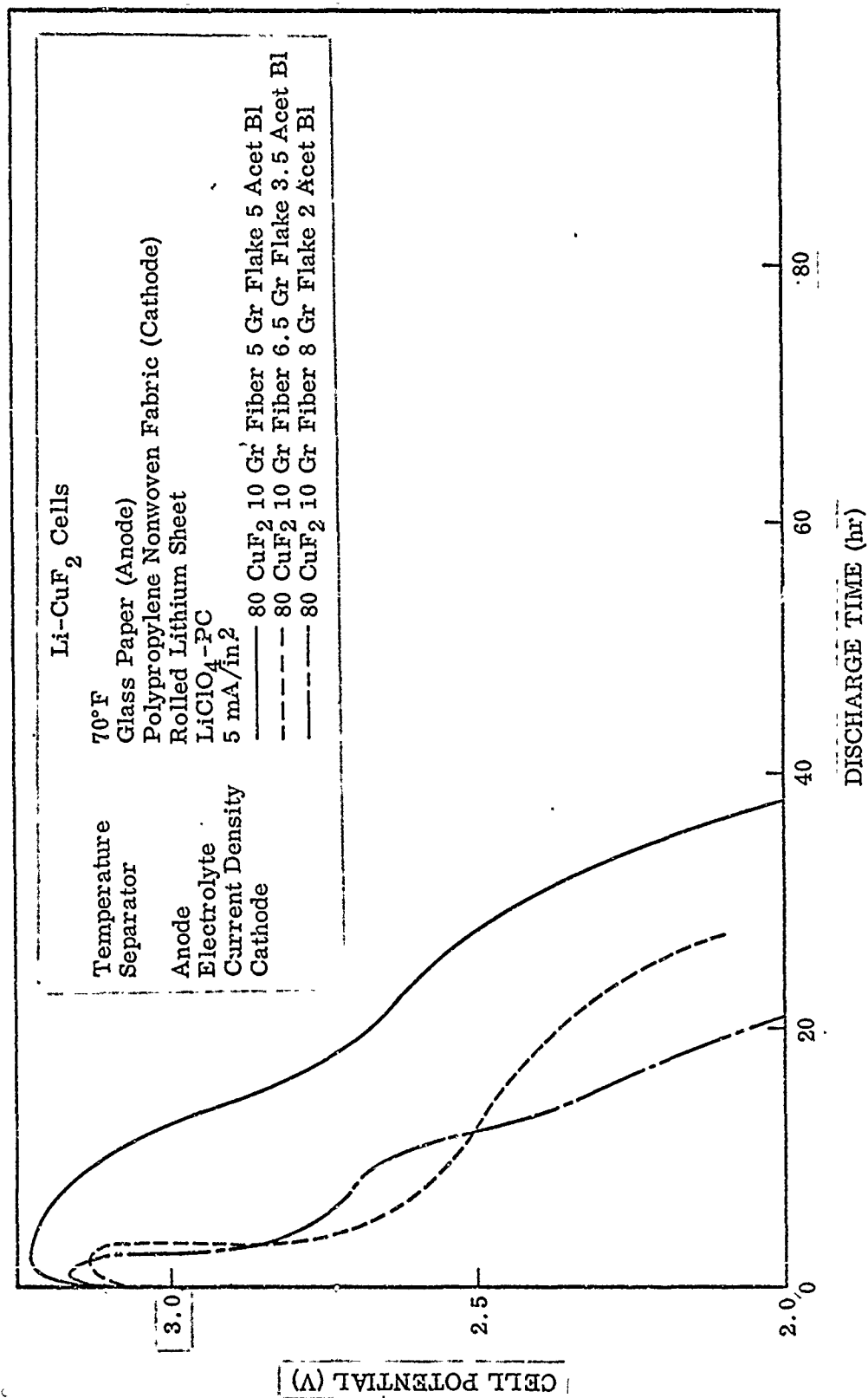


Fig. 8 Discharge of Cells With Different Amounts of Acetylene Black in the Cathode

grid; if no soluble copper ion is present, connection must be made between the  $\text{CuF}_2$  crystal and solid conductive material which is electronically connected to the grid. Soluble copper reduces the actual current density by making a much larger conductive structure available for reaction. The higher discharge voltage curves with wet material in the cell can be the result of reduced effective current density in the cathode. It is conjectured that where there are no soluble copper species, a critical amount of conductive material must be present to maintain conductive paths through the solid cathode structure to the grid; with lesser amounts some of the conductive particles are isolated and the effective electrode is reduced.

#### 2.4 ANODE POLARIZATION TESTS

One of the milestones of this contract is the fabrication of an anode that may be discharged for 100 hr at  $10 \text{ mA/in.}^2$  with less than 100 mV polarization. Previous attempts to achieve this milestone have been unsuccessful because available cathodes could not be discharged at this current density for this length of time in the electrolyte used in the cells. A cell with a lithium anode and an inert nickel cathode was assembled with a power supply to drive the discharge at a constant current. The electrodes were of  $3 \text{ in.}^2$  area and were positioned horizontally with the inert cathode on the bottom. About 1.5 in. separated the two electrodes which were contained in a glass fitting with a gasketed Teflon cover which also carried the electrical leads. The electrode leads were insulated and the polarization of the anode was measured with a lithium wire reference electrode contained in a polyethylene tube drawn into a capillary and located in proximity to the anode. Readings of the anode-cathode voltage and anode-anode reference voltage were taken every hour. A constant current power supply was used to maintain the current at  $10 \text{ mA/in.}^2$ . In addition, every 12 hr the current was changed to  $33 \text{ mA/in.}^2$  and then in a series of steps to zero current, back to the maximum current and finally to the steady current rate. The polarization at the highest current rate was too high for the recorder span.

A first test ran 80 hr before premature exhaustion of the lithium anode, presumably because of air leakage. An average of the increasing and decreasing step values

corrected for the lithium-lithium reference value at open circuit for a second more successful effort is plotted on Fig. 9. As can be seen, the polarization is relatively constant with time at lower current densities. The increase with time for the higher current densities may be the result of changing lithium surface, or changing contact with its supporting grid. The initial increase in polarization may be the result of surface film on the lithium electrode. Over 100 hr of discharge at 10 mA/in.<sup>2</sup> were obtained on this test with less than 100 mV polarization, a successful realization of one of the contract milestones.

## 2.5 CELL DISCHARGE EQUIPMENT

Bag-type cells constructed as previously described have been used to evaluate electrode variables by discharging them in series with a constant current power supply which maintains a steady current discharge. Upon occasion, a cell which loses capacity prematurely may have a reversed potential placed across its terminals that may be great enough to result in deposition of spongy lithium on the electrode normally cathodic. In one case, this resulted in a short circuit which developed enough heat to start a fire which in turn ignited other cells. To prevent this in the future, the present practice is to mount all cells on a cement-asbestos board fixture which in turn plugs into a stainless steel holder with room for ten cells. To prevent harmful cell reversal, a diode (1N91) is connected across the battery terminals. This offers several megohms resistance with normal cell polarity but carries the current when the potential is reversed about 0.2 V. Figure 10 shows the single cell fixture with diode in place as well as the ten cell holder.

## 2.6 ALUMINUM CASED 25 A-HR CELL AND BATTERY TESTS

### 2.6.1 Cell Discharge Tests

Four aluminum cased 25 A-hr cells were assembled with seven cathodes prepared by standard procedure with 2.5 g of Source A  $\text{CuF}_2$  and eight anodes of rolled 0.022-in. lithium. The electrode grids were of expanded metal 0.005-in. thick, rickel for the

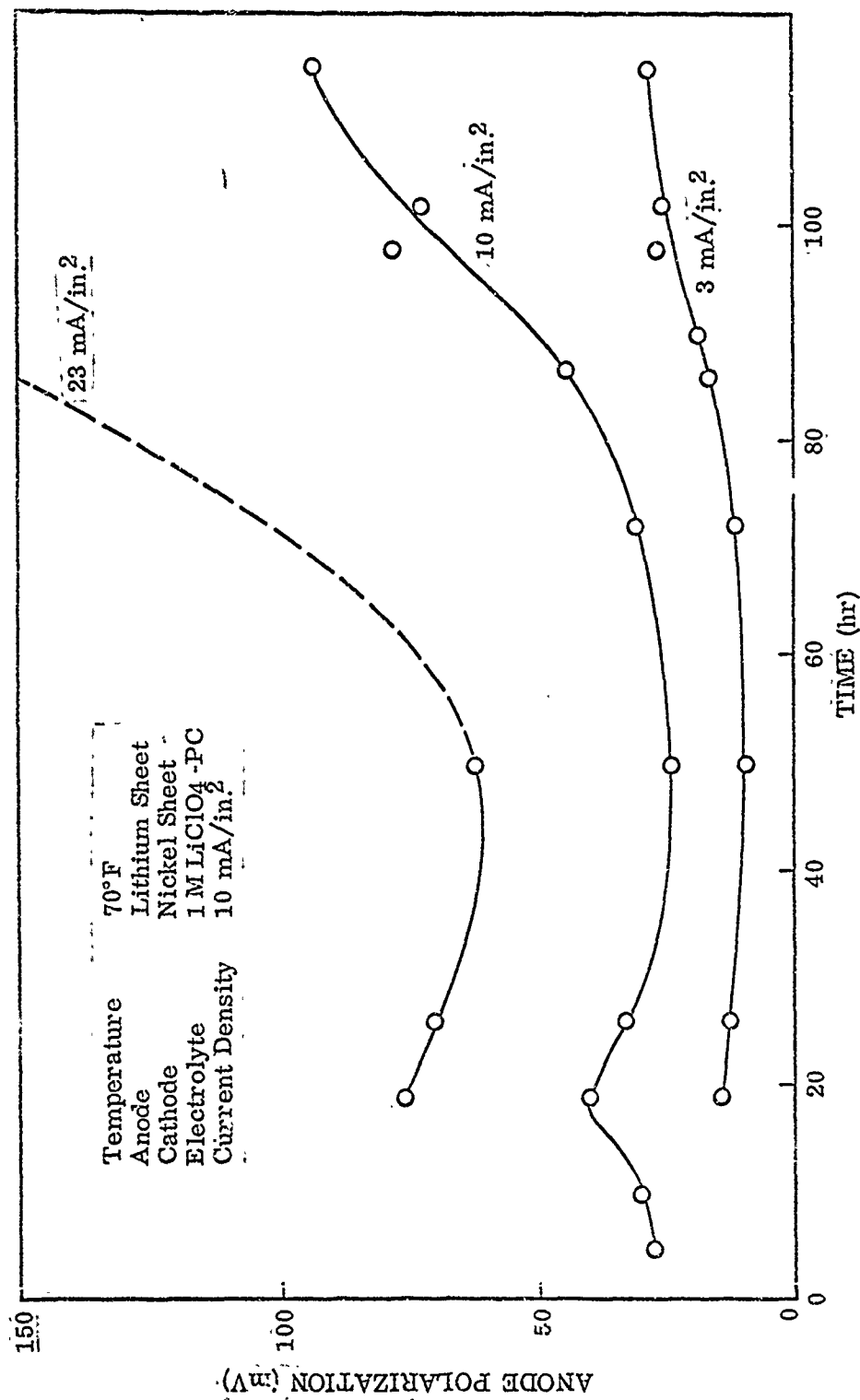


Fig. 9 Polarization of Sheet Lithium Anode



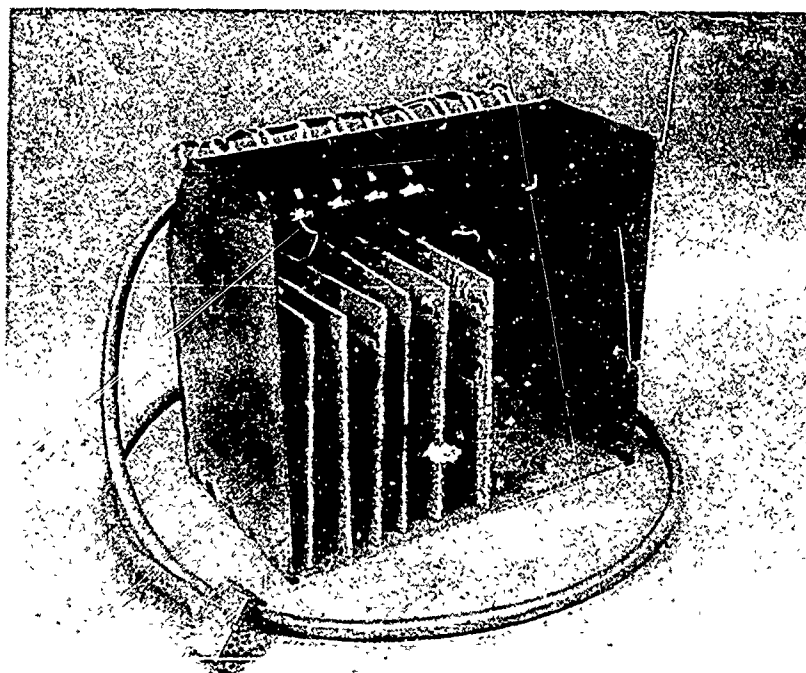
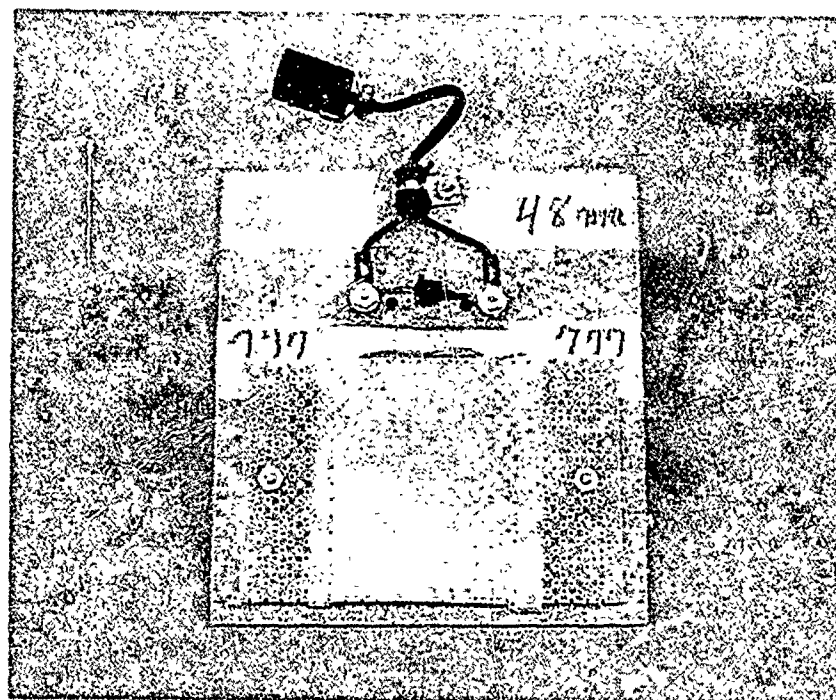


Fig. 10 Cell Discharge Fixtures

anode and copper for the cathode. The grids were reinforced by spotwelding 0.002 in. sheet stock of nickel or copper across the top edge of the electrode and over the tab. Glass and cellulose paper separators were used on the anodes and cathodes respectively. The discharge of Cells 848 and 849 is shown on Fig. 11 and Cell 851 on Fig. 12. Cell 850 was to be used for a calorimeter test but evidently shorted (as evidenced by heat in the calorimeter) during the night while on open circuit. None of the cell discharges were satisfactory with the best cell (Cell 851) delivering 15.5 A-hr to a 2.0 V endpoint. The cells weighed 363 to 376 g without electrolyte and 470 to 472 g after filling. Post mortem of cells showed copper deposition on the lithium anode and heavy lithium corrosion. All of these cells became swollen and required release of pressure during discharge.

Four more cells were assembled with Source A  $\text{CuF}_2$  in the cathodes and similar to the previous four except for polypropylene nonwoven fabric separators on the cathode. One cell of this group (Cell 871) evidently shorted before it could be placed on discharge. The other three cells were discharged at 350 mA. All three cells discharged initially above 3.0 V but all had a falling voltage which dropped abruptly to below 1.0 V after 30 hr of discharge. All of these cells swelled from gas pressure and were vented periodically. On post mortem, the anodes and anode grids had deposits of copper. The cathodes were copper colored on the outside but black below the surface. The electrolyte contained suspended solid matter. The cells had been filled in steps by partially filling the cells with electrolyte and evacuating them in the glove box ante chamber. This removed gas rapidly and it was thought that the vigorous evolution of gas had eroded the cathodes and the suspended graphite had caused partial shorting. In addition, water introduced in the cathode and in the electrolyte reacted with the lithium to form hydrogen as well as solubilized the  $\text{CuF}_2$  so it could diffuse to the anode for reaction. The swelling which resulted from the gas pressure may have contributed to shorting by extrusion of cathode mix as the case was warped or by cutting through the separator.

Two cells were then prepared with a polypropylene fiber separator heat sealed around the cathode to form a bag. Cell 880 had Source A cathodes and those in Cell 881 were prepared from Source B  $\text{CuF}_2$ . An effort was made to fill these cells without abrupt

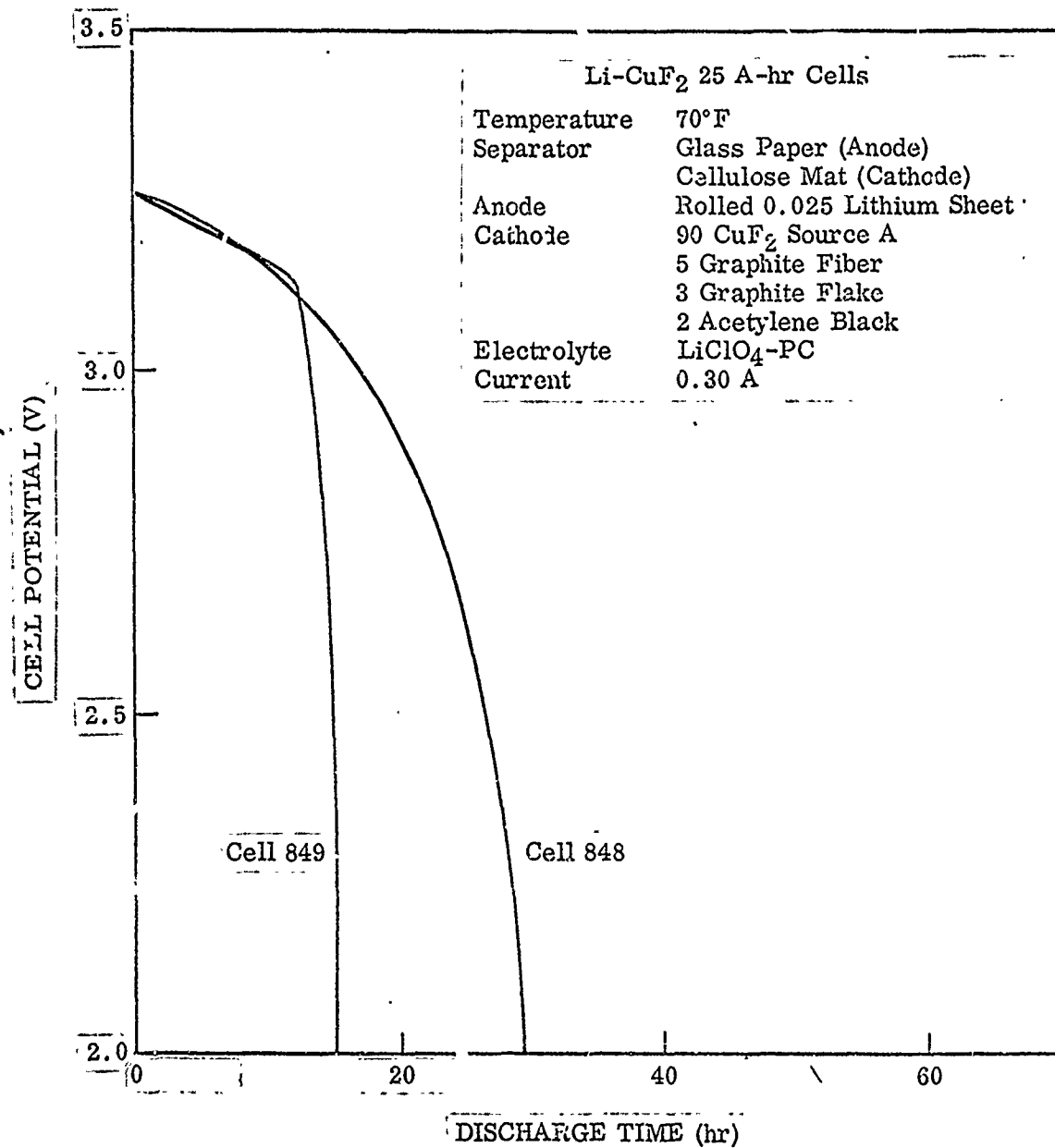


Fig. 11 Discharge Test of Cells 848 and 849

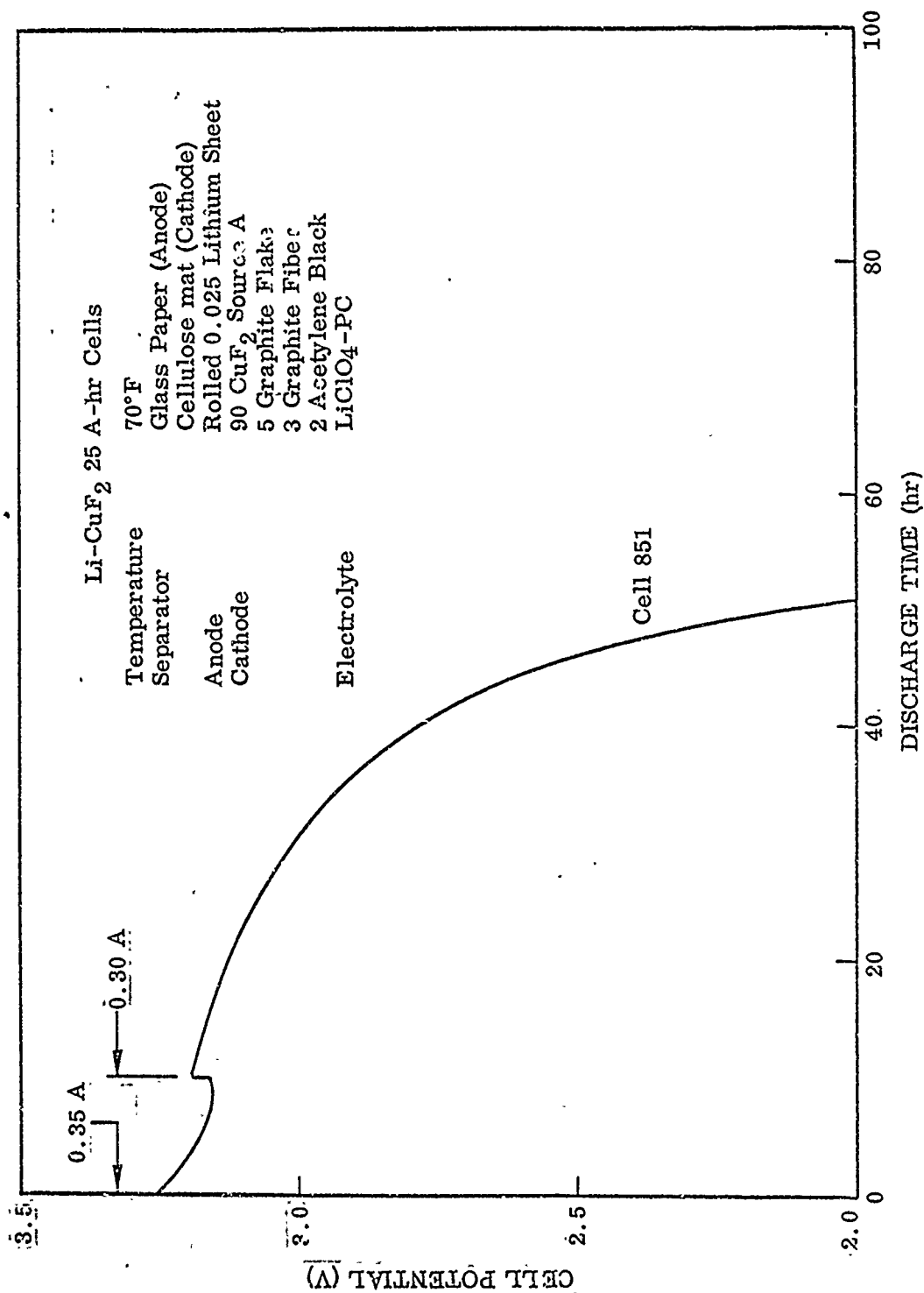


Fig. 12 Discharge Test of Cell 851

exposure to vacuum. Cell 881 was given short discharges in the calorimeter and was then discharged at 300 mA as shown on Fig. 13. It was removed after 90 hr for additional calorimeter testing and then returned to discharge. The cell was clamped between plates during discharge and was vented at the end of 16 hr but showed no indication of pressure afterward and there was no case distortion. It discharged 27.9 A-hr above 2.0 V and delivered 68.0 W-hr/lb of total cell weight. Cell 880 was held overnight on open circuit and was found badly swollen in the morning without open circuit voltage. It had evidently shorted as the result of case distortion.

Cell 882 with Source B  $\text{CuF}_2$  and Cell 883 Source A  $\text{CuF}_2$  were prepared with bagged cathodes and additional tab spacers to prevent excessive tab bending. They were filled in a fixture that allowed slow evacuation and were evacuated before electrolyte was added. Cell 883 was to be used for calorimeter discharges but showed heat generation while on open circuit in the calorimeter. It was removed and discharged in series with Cell 882 at 350 mA corresponding to 2.8 mA/in.<sup>2</sup> of electrode. The discharge curve of these two cells is shown on Fig. 14. Cell 882 delivered 32.2 A-hr to a 2-V endpoint and had an energy density of 72.5 W-hr/lb of total cell weight.

#### 2.6.2 Heat Production in Li- $\text{CuF}_2$ Cells

The heat produced by a cell under discharge was measured using the calorimetric apparatus described previously. The cell (No. 881) was prepared from rolled lithium anodes, 90% copper fluoride Source B cathodes and 1 M lithium perchlorate-propylene carbonate electrolyte and was housed in a sealed aluminum case. The average open circuit voltage for the runs was 3.425 V at 25 °C which corresponds to a free energy value of -79 kcal/equiv. The average heat of reaction calculated from the heat produced and the operating cell voltage was -78. kcal/equiv. These values are the same as those previously reported for a cell run with lithium and copper fluoride electrodes with sodium hexafluorophosphate-propylene carbonate electrolyte. The heat rate in watts was measured at various currents and the data is summarized in Fig. 15.

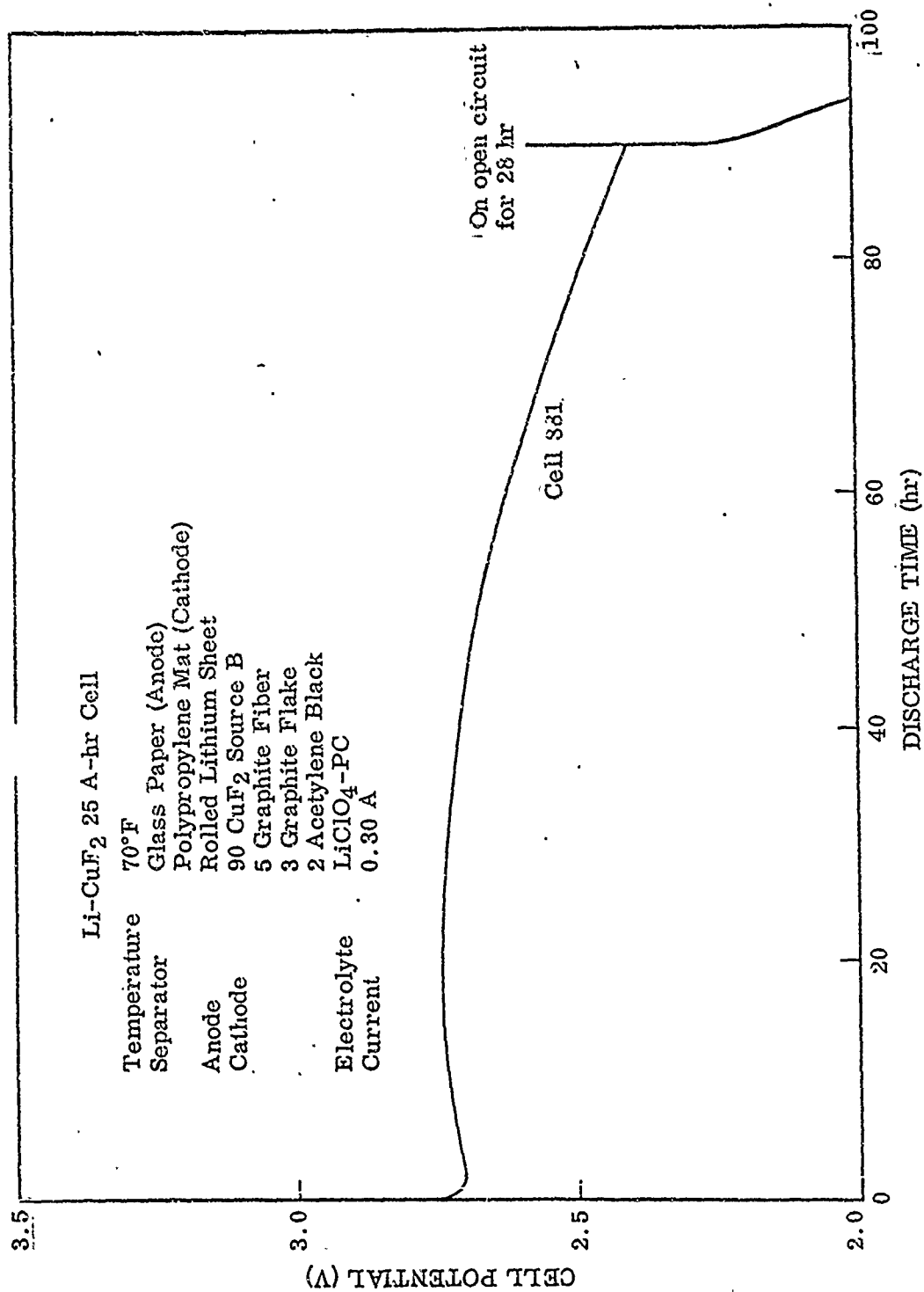


Fig. 13 Discharge Test of Cell 881

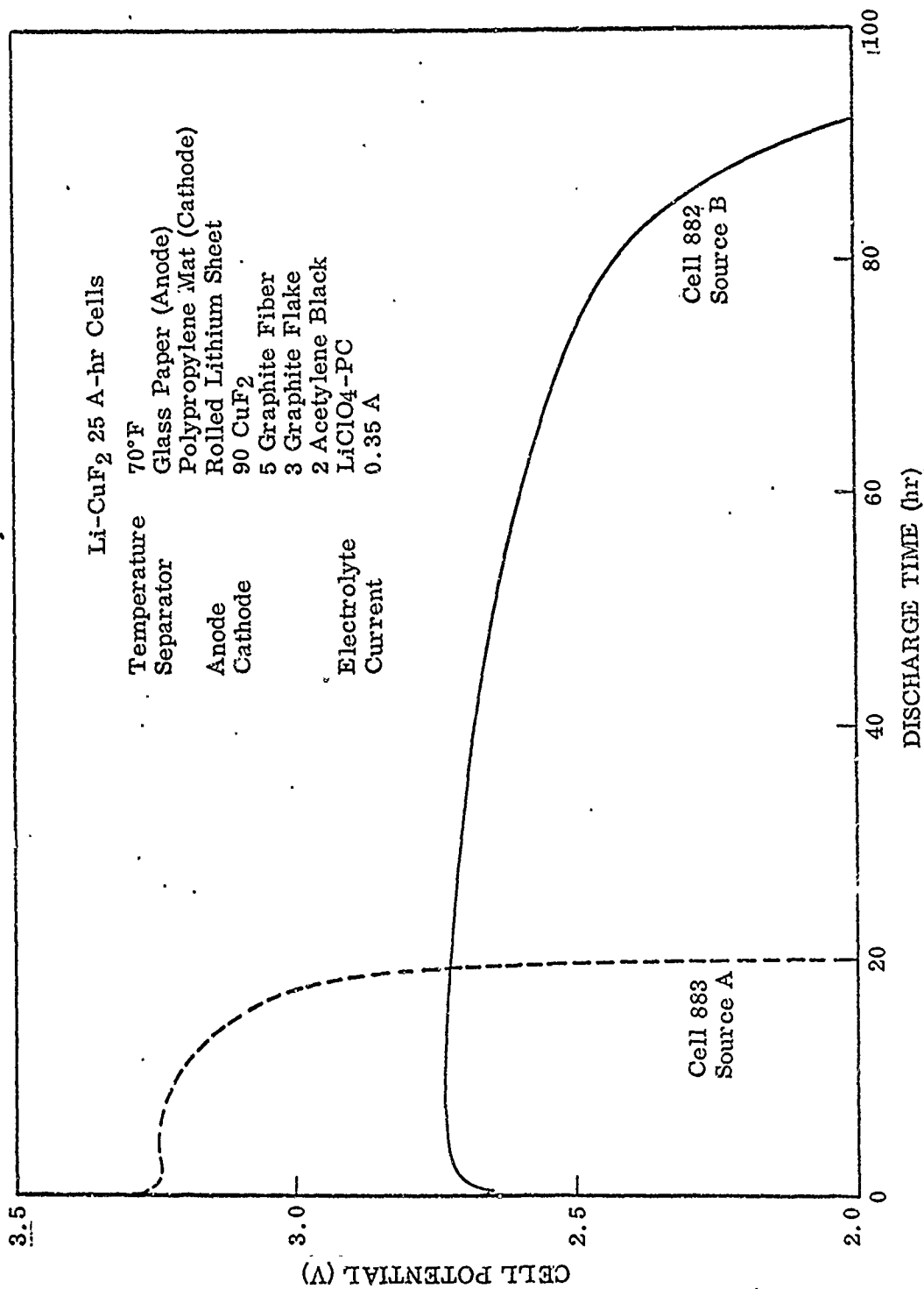


Fig. 14 Discharge Test of Cells 882 and 883

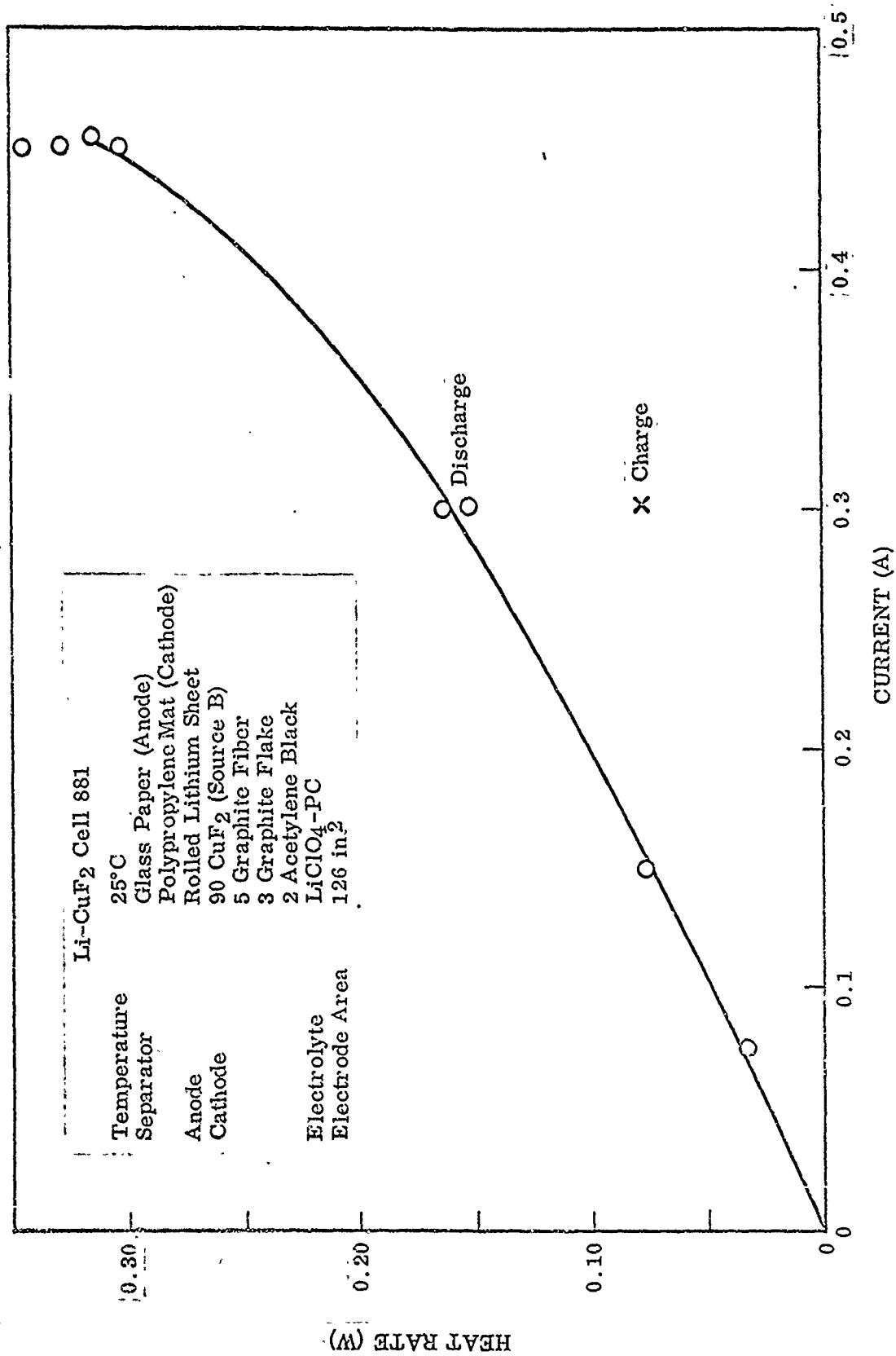


Fig. 15 Heat Production in a Lithium-Cupric Fluoride Cell



## 2.7 30-V BATTERY TEST

Nine cells of the nominal 25 A-hr aluminum cased type were assembled, series connected and discharged as a battery. The anodes were of lithium strip rolled on one side of 3/0 expanded nickel sheet. The cathodes were made from a mix consisting of 80% Source B  $\text{CuF}_2$ , 10% graphite fiber, 6% graphite flake and 4% acetylene black. This preparation was mixed in a blender and filtered in two steps on a filter with an area sufficient for four electrodes. A 3/0 expanded copper sheet was inserted into the filter between the two filtering steps for central location of the grid in the cathode. The cathodes were cut to size and pressed in plastic bags with absorbing material at about 1000 lb/in.<sup>2</sup> The cells were assembled with glass paper separators on the anodes and polypropylene nonwoven fabric (PC-F7181) on the cathodes. The bottom of the aluminum cans was welded into place and the cells were filled in a vacuum filling apparatus with 105 ml of 1.0 M  $\text{LiClO}_4$  in propylene carbonate. Seven anodes and six cathodes were used in each cell with a total active area of 108 in.<sup>2</sup> Weight of the cells after filling ranged from 439-480 g and open circuit voltage from 3.398 to 3.452 V. The battery shown in Fig. 16 weighed 9.18 lb and its open circuit voltage was 30.93 V. The battery was discharged at a 0.30-A rate which was the equivalent of 2.8 mA/in.<sup>2</sup> with the discharge curve shown on Fig. 17. The short discharge was the result of individual cells losing voltage abruptly. This was usually associated with gassing and some heating. The cells were vented during discharge and end clamping plates were added after 24 hr of discharge. The discharge life of the individual cells ranged from 30 to over 100 hr to a 2.0-V endpoint. The battery delivered 9 A-hr with an energy to weight ratio of 24.5 W-hr/lb to the specified endpoint of 22.0 V. The best cell discharged for 26.5 A-hr and delivered 66 W-hr/lb to a 2.0-V endpoint. Utilization of  $\text{CuF}_2$  in this cell was 42.5%. The power supply controlling current discharge changed to a voltage regulation mode after 45 hr of discharge and current after this time was below 0.30 A.

Premature failure of cells was the result of shorting. This in some cases was the result of case swelling with consequent electrode misalignment. In other cases, it

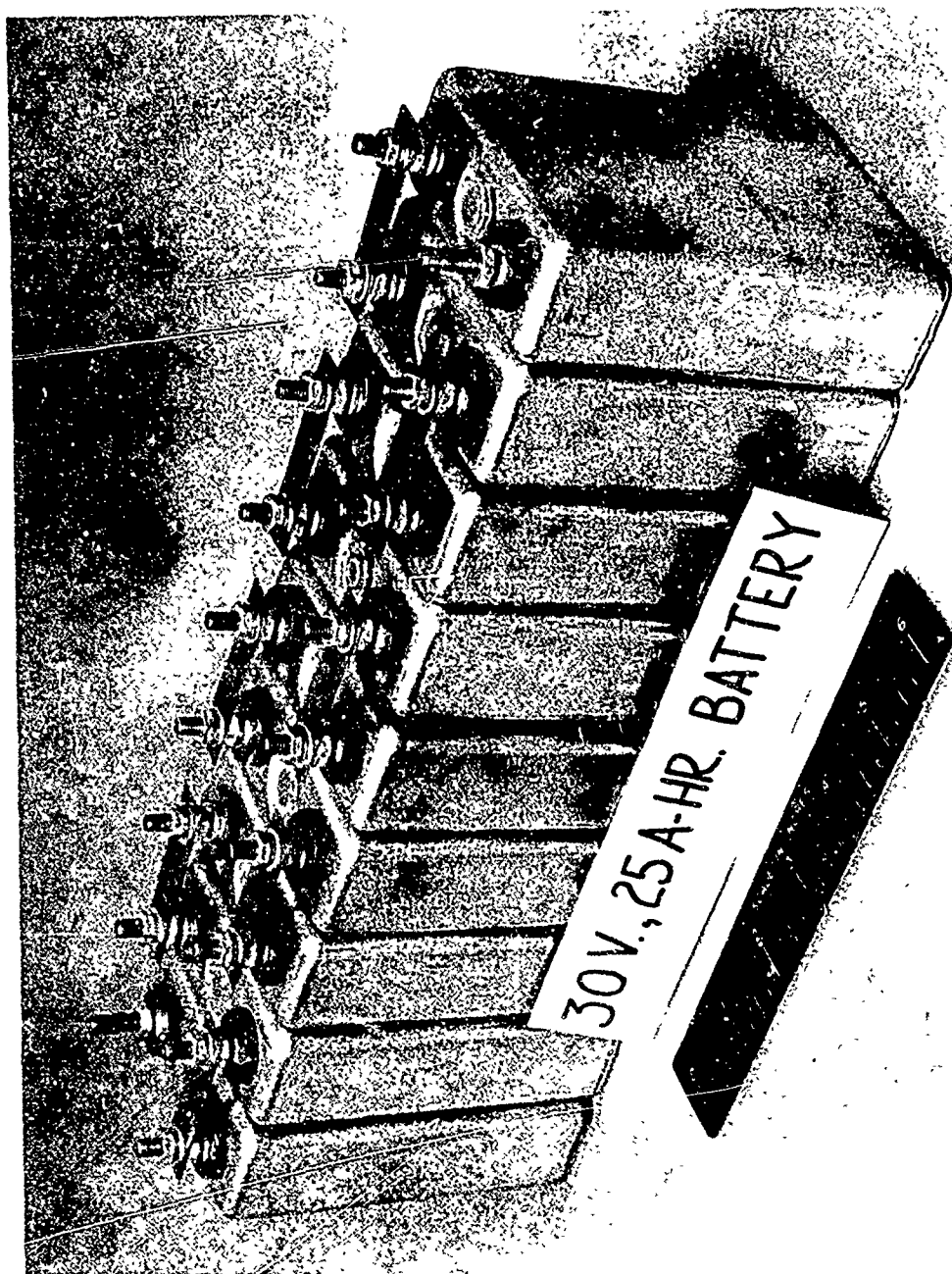


Fig. 16 30-V Battery

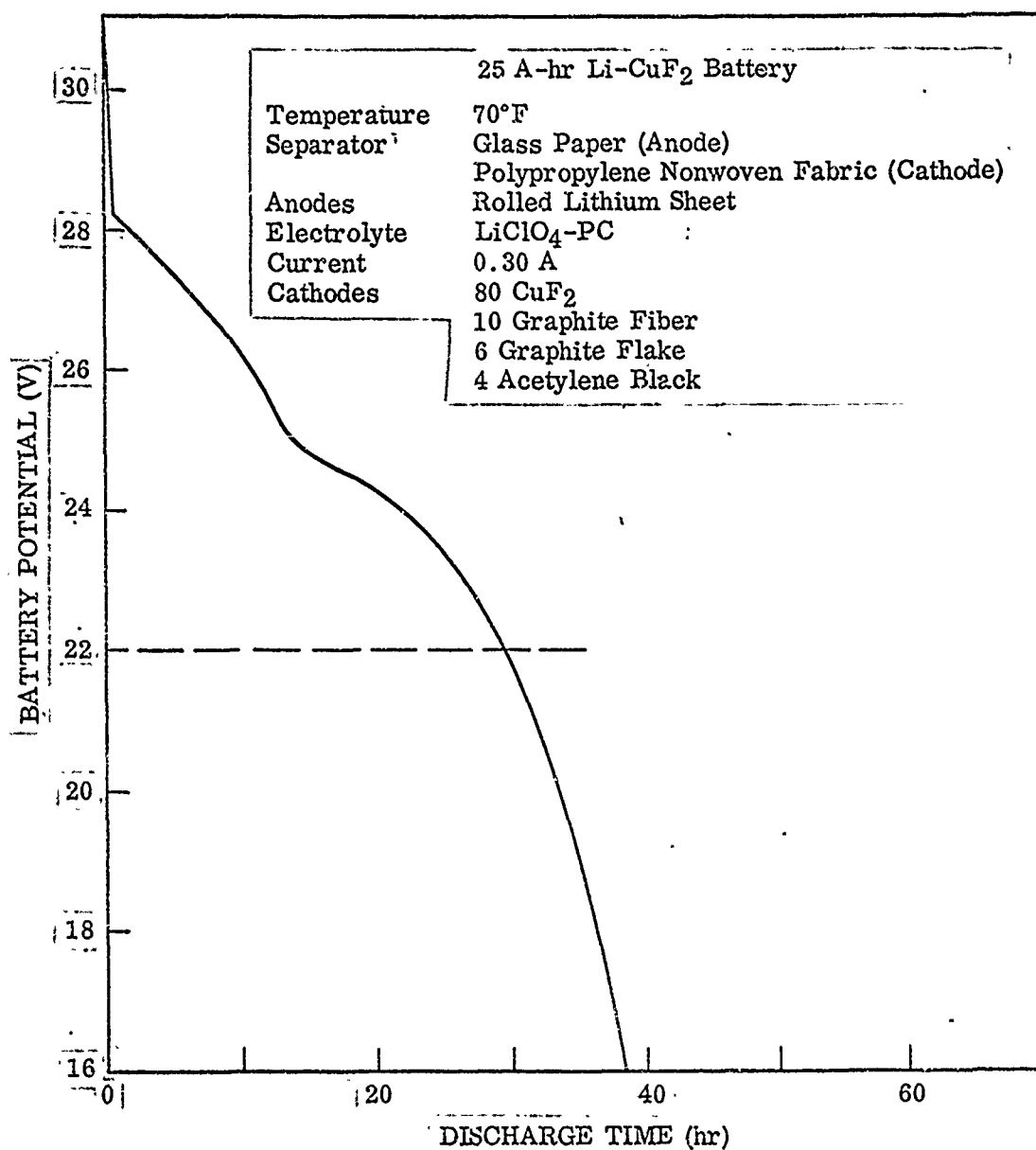


Fig. 17 Discharge of Aluminum Cased 30-V Battery

may have been because of cathode extrusion. The cathodes were uneven because of the necessity of fabricating large quantities in as short a time as possible. In some cases, storage of a day was required before assemble and there may have been some water absorption. There appeared to be no correlation between open circuit voltage and failure. The two heaviest cells were in the three that failed first although this is probably not significant.

In a later analysis of the electrolyte which had been used in these cells, it was discovered that the water content was 1000 ppm. This was the result of using lithium perchlorate which had been received as anhydrous but was hydrated. A much larger amount of water was removed during drying than with the usual material and a longer time was used for drying, but evidently material under the surface of the salt in the drying flask did not get completely dry.

The results of this battery test inadvertently parallel that experienced with the aluminum cased cell tests when Source A  $\text{CuF}_2$ , which has a higher water content, was used in the cathodes. Evidently, these effects are not as obvious in plastic cased cells where there is greater opportunity for pressure release by gas leakage.

### Section 3 FUTURE WORK

During the next work period, it is intended that additional time be spent in further optimizing the cathode composition and fabrication technique. Additional aluminum cased cells will be constructed and tested with a special effort to maintain a low water content in the cell; 30-V batteries will be constructed as the test results from single cell indicate that more efficient  $\text{CuF}_2$  utilization and a better power to weight ratio may be obtained.

A laminated plastic case will be developed to test design ideas that may be used in 1500 A-hr cells and batteries, the construction of these larger batteries being a major goal of this program.

Appendix  
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